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A Side Reaction Giving Rise to Cross-Linking in the Preparation of Poly Pyromellitimides*

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Dedicated to Prof. Dr. H. A. STUART on the occasion of his 65th birthday

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SUMMARY:

The paper deals with difficulties experienced according to the patent literature in the preparation of linear soluble polymers of poly pyromellitimides from pyromellitic acid and diamines.

It is suggested that diamidation which will, on theoretical grounds, always occur as a side reaction in imide formation, is probably the main cause of these difficulties as it gives rise to branching and cross-linking.

The equilibrium reactions involved are discussed and it is shown that a slight excess of basic groups will promote, and a slight excess of acid groups supress the side reaction. These conclusions are underlined by experiment.

The magnitude of the equilibrium constants of the elementary reactions in question are determined approximatively from the investigation of non-polymeric model systems in which pyromellitic acid is substituted by *ortho*-phthalic acid.

ZUSAMMENFASSUNG:

Es wird der Grund für die in der Patentliteratur beschriebenen Schwierigkeiten bei der Herstellung von löslichen linearpolymeren Polypyromellitimiden aus Pyromellitsäure und Diaminen diskutiert.

Dabei wird dargelegt, daß die Diamidierungsreaktion, welche theoretisch immer als Nebenreaktion bei der Bildung von Imiden auftreten wird und zu Verzweigung und Vernetzung Anlaß gibt, wahrscheinlich als Hauptgrund dieser Schwierigkeiten anzusehen ist.

Die einschlägigen Gleichgewichtsreaktionen werden diskutiert, und es wird geschlossen, daß die Nebenreaktion von einem kleinen Überschuß basischer Gruppen gefördert und von einem kleinen Überschuß saurer Gruppen unterdrückt wird. Diese Folgerung wird durch Experimente gestützt.

Die Gleichgewichtskonstanten der betreffenden Einzelreaktionen werden annähernd bestimmt durch Untersuchung von Modellsystemen nicht polymerer Art, in denen die Pyromellitsäure durch Orthophthalsäure ersetzt worden ist.

1. Introduction

Five-membered cyclic imides, as formed from aliphatic dicarboxylic acids or from aromatic ortho-dicarboxylic acids and a primary amine, are

^{*)} Communication Nr. 124.

stable and rigid cyclic structures which might well be of interest as building blocks in polymers. Such polymers can be prepared by reacting bis-1.2 or bis-ortho-dicarboxylic acids with diamines and they represent polyimides.

Though mentioned in the patent literature as early as 1942^{1} , polyimides have not yet made great strides in the polymer field. In the search for polymers which will retain good mechanical properties at elevated temperatures, as beyond 130-140 °C., interest in polyimides was revived about a decade ago and focussed in particular on those derived from pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) in combination with diprimary aliphatic amines. Thus, polymers of the type:

exhibiting high softening and melting points were prepared. In order to obtain polymers with practical processability, n should at least have the value 9 (the octamethylene diamine analog having a melting point beyond 400 °C. and degrading at this temperature). Also other not readily available diamines as, e.g., 4.4'-dimethylheptamethylene diamine were recommended²). However, polyimides prepared by polycondensation from the "nylon-salts" of the acid and the diamine, or from either the tetraalkylester of the acid or from the acid dianhydride by reacting with the diamine, exhibited the tendency to give brittle, obviously branched or cross-linked products. More favourable results were claimed in the polycondensation of the "ester salts" prepared from dialkylesters of pyromellitic acid with one molecule of the diamine³). Even then very special procedures in the preparation and the processing of the polymer seem to be required in order to arrive at valuable non-brittle products.

Examination of the chemical reactions involved reveals that in the preparation of polyimides a side reaction giving rise to branching and cross-linking will always have to be accounted for, since — in theory — amide formation will always compete with imide formation. With regard to the latter the dicarboxylic acid group is monofunctional while it is difunctional with regard to the former. Amid formation will give rise to branching of the type



and thus may, eventually, also lead to cross-linking.

The extent of cross-linking in the equilibrium product will depend on the relative magnitude of certain equilibrium constants (see below).

Reading the patent literature leaves one with the conviction that amide formation as a side reaction, though not specifically mentioned there, has been one of the main stumbling stones in the preparation of valuable polyimides.

It seemed of interest to study the various recations involved somewhat closer and to ask what could be done to minimize the undesired side reaction.

2. Reactions involved in imide-formation

The equilibrium reactions in question can be represented thus:



To arrive at expressions for the equilibrium constants, we set:

f conc. of *ortho*-diacid groups m conc. of monoamide groups d conc. of diamide groups i conc. of imide groups

and then arrive at

$$K_m = \frac{mw}{2fa}$$
 (1) $K_i = \frac{2iw}{m}$ (2) $K_d = \frac{2dw}{ma}$ (3)

The numerical coefficients are chosen so as to consider elementary reactions of one functional group or of one C-N bond in the imide.

The equilibrium constant of the reaction

$$(\bigcirc CO \\ CO \\ CO \\ CO \\ NR + RNH_2 \iff (d) K_{di}$$

depends on K_d and K_i:

$$K_{di} = \frac{d}{ia} = K_d/K_i$$
 (4)

The degree of branching and cross-linking is related to the proportion of diamide to imide formation, given by

$$\frac{\mathrm{d}}{\mathrm{i}} = \frac{\mathrm{K}_{\mathrm{d}}}{\mathrm{K}_{\mathrm{i}}} \cdot \mathrm{a} \tag{5}$$

It thus depends on the ratio K_d/K_i and is proportional to the NH_2 -group concentration.

This leads to the important conclusion that in the equilibrium product the concentration of NH_2 -groups should be kept as low as possible, e.g., limitation of molecular weight should be achieved by a slight excess of the acid component.

For practical application of the Equations (1) to (4) it should be accounted for that K_i and K_{id} have a dimension. Introducing, for convenience, mole/kg. as a unit of concentration, Equations (3) and (4) should read:

$$K_1 = \frac{2iw}{gm} \quad (5a) \qquad \qquad K_{di} = \frac{gd}{ia} \quad (4a)$$

where g = total weight of the system in kg.

To arrive at the numerical value of (5), K_d/K_i must be determined by experiment. From work described below follows that K_d/K_i is of the order 0.1.

In a polycondensate starting from 1 mole of pyromellitic acid and 1 mole of a diamine with a mol. wt. of, e.g., 150, the initial concentration of the components will be $n_0 = N_0/g = 2.5$ mole per kg. (see section 4). The equilibrium degree of polymerization is given by $2n_0/a$ (see Eq. (8a)). Considering the preparation of a polymer with $P_n = 150$, the concentration of amine groups will be of the order 5/150 = 0.03. The proportion d/i of side to main reaction will then be of the order $0.1 \cdot 0.03 = 0.003$ or as 1 to 300. Out of two molecules one will be branched.

Taking into consideration that branching can be reduced by using a slight excess of acid to limit the DP to 150, it would seem possible to keep branching and cross-linking at an acceptable level and to prepare completely soluble polyimides by polycondensation. This is born out by experiment which, however, reveals practical complications of another kind (see section 3).

3. Poly pyromellitimides from hexamethylene diamine (HMD) and nonamethylene diamine (NMD)

"Nylon-salts" of pyromellitic acid (PMA) with both diamines in the molar proportion 1:1 can be readily prepared in good yield. Upon heating in open melting point capillaries, both salts begin to lose water at about 200 °C. On further raising the temperature, no signs of melting or softening are observed in the case of HMD up to 390 °C., and the product is completely insoluble in *m*-cresol. In the case of NMD a homogeneous melt is obtained at 320-330 °C. and the product is partly soluble in *m*-cresol.

More carefully conducted experiments, when heating is carried out in vacuo at 250 °C. and with a somewhat larger amount of salt, showed the following results:

The HMD-salt lost 20.5% of its weight in 1 hr (calcd. loss of water 19.5%). No further change in weight is observed and the powdery product is completely insoluble in *m*-cresol.

A similar result was given by the nylon-salt prepared from the dibutylester of PMA and HMD. The loss in weight amounted to 41.8% (calc. for loss of water and butanol 38.2%).

The nylon-salt of PMA with NMD lost 16.8% of its weight in 1 hr. under the same conditions (calcd. 17.4%). The product was only partly soluble in *m*-cresol. It melted at 280–290 °C. and resolidified with crystallization at 267 °C. (hot stage microscope). On a hot plate of 300–305 °C. surface temperature it could be pressed to a moderately tough film. Upon heating in *m*-cresol the film left a gelatinous insoluble residue.

In the case of NMD, further experiments showed that perfectly soluble polymer can be prepared provided that the heating of the nylon-salt is performed so as to exclude escape of volatile products. First a pre-condensate was prepared by heating the salt in N₂-vacuo for 2 hrs. 254 °C. On cooling a light yellow solid and a small quantity of water were obtained. The solid was powdered and washed with dry acetone. It was completely soluble in *m*-cresol and melted under the *Kofler* microscope between 278-286 °C. A portion of it, after heating for half an hr. at 350 °C. in an evacuated sealed tube, was still completely soluble in m-cresol to a viscose solution.

If, however, the second heating was carried out in a scaled tube which partly emerged from the heating block, a trace of solid deposited or the cold part of the tube as a sublimate which could be identified as the dianhydride of PMA. The polymer was still soluble in *m*-cresol. Contrarily, if the same experiment was repeated in a tube which was connected to a vacuum pump, then the quantity of sublimate was much larger and again consisted of PMA di-anhydride. It contained no NMD (ninhydrin test). The polymer was now insoluble in *m*-cresol forming a gelatinous mass with this solvent.

These experiments show that the pre-condensate tends to give off pyromellitic acid di-anhydride as a volatile component. This will entail an excess of basic groups in the polymer and promote cross-linking. In the condensate still another reaction has to be accounted for:



competing with imide formation.

It is remarkable that in the case of HMD under no circumstances a soluble polymer could be produced. This curious fact remains to be explained.

Whereas in the preparation of polyamides of the nylon type from aliphatic dicarboxylic acids, attention must be given to the volatility of the diamine component in the polycondensate, the preparation of polyimides from PMA has to face the volatility of the acid component in the form of its anhydride. That in the latter case the diamine component does not show a tendency to escape by evaporation is probably due to the much stronger acidity of the *ortho*-dicarboxyl group as compared to that of the aliphatic carboxyl. This is corroborated through the fact that the aqueous solution of the nylon-salts of PMA has a $p_{\rm H}$ of 3.9 in contrast to that of solutions of nylon-salts of the aliphatic acids with a $p_{\rm H}$ of 5.5–6.

4. Determination of equilibrium constants

Since quantitative investigation of equilibria in polymer polycondensates is very difficult on account of the low concentration of the functional groups which must be determined analytically, we have chosen to investigate systems with *ortho*-phthalic acid as model systems which can be expected to yield quite comparable results. Using di- or monofunctional amines, polymerization is either almost or entirely absent. As a mono-amine, n-octylamine was selected.

Mono- and dioctylammonium phthalates can be readily prepared (see exp. part) and represent analoga to the nylon-salts of bifunctional amines.

The equations pertaining to equilibrium products can be derived as follows.

starting system consist of	
$\mathbf{N_0}$ mole phthalic acid	initial conc. n _o
$2\mathrm{bN_0}$ mole monoamine	initial conc. 2 bn _o
\mathbf{W}_{0} mole water	initial conc. w _o

then the boundary conditions are

Let the

(6.1) $w = w_0 + m + 2d + 2i$	(water concentration)
(6.2) $f = n_0 - m - d - i$	(conc. of free phthalic acid)
(6.3) $c_m = m$	(conc. of COOH in monoamide)
(6.4) $c_f = 2f$	(conc. of COOH in phthalic acid)
(6.5) $c = c_f + m$	(conc. of total COOH)
(6.7) $c_1 = 21$ (6.5) $c = c_f + m$ (6.6) or $c = 2n_0 - m - 2d - 2i$ (6.7) $a = 2bn_0 - m - 2d - i$	(conc. of total COOH) (conc. of total COOH) (conc. of NH ₂ groups)

Only (6.1), (6.2), (6.6), and (6.7) are independent equations. At least three of the unknowns must be experimentally determined in order to solve the problem. We select a, c, and f. The other unknowns are then given by the equations

(7.1)	i	=	$2n_0(1-b) - (c-a)$	(from 6.1 and 6.6)
(7.2)	\mathbf{w}	=	$w_0 + 2n_0 - c - w_0 + 2bn_0 - a + i$	(from 6.1 and 6.6)
(7.3)	d	==	$f - a - n_0(1 - 2b)$	(from 6.2 and 6.7)
(7.4)	\mathbf{m}	=	$\mathrm{c}-2\mathrm{f}$	(from 6.5)

In the case of phthalic acid and a diamine and the initial system consisting of:

we can use exactly the same equations. In this case some degree of polymerization can occur. The degree of polymerization of the product can be easily calculated to be:

$$P_n = (1 + b)/(1 - b + a/n_0)$$
(8)

and in the case of b = 1 (nylon-salt) this simplifies to

$$\mathbf{P_n} = 2\mathbf{n_0}/\mathbf{a} \tag{8a}$$

To achieve the goal of determining f, c, and a (or, alternatively, f, m, and a) in equilibrium products, potentiometric titrations in a solvent consisting of a mixture of benzylalcohol and methanol in the volume proportion of 3:1 were found to be applicable (see exp. part).

In systems containing water as equilibrium products from mixtures of phthalic acid with a mono- or diamine the accuracy of the analysis was only sufficient in products with a not too low content of free phthalic acid and this considerably restricted the free choice of the starting mixture. Among numerous determinations on numerous systems, only one yielded results which we considered accurate enough to arrive at the correct value of equilibrium constants.

A mixture of 2.000 mmole nylon-salt phthalic acid-HMD with 2.0139 mmole free phthalic acid was heated in a sealed vessel for 3 hrs. at 200 °C., then rapidly quenched and dissolved in the afore-mentioned solvent for potentiometric titration. The result was (expressed as concentrations in mequiv./g.):

f = 0.0479	(free phthalic	acid)
c = 0.1064	(total carboxy	vl)
a = 0.0126	(free amino gr	oups)
Further, we have:	$N_0 = 4.0139$	(mmole total initial phthalic acid)
	$bN_0 = 2.000$	(mmole diamine) and, hence,
		b = 0.4983
	g = 0.898	(weight of total substance in g.)

from which follows: $n_0 = 4,469 \text{ mmole/g. or mole/kg.}$

Equations (7.n) then give:		Out of 100 mole phthalic acid are transformed into:	
m = 0.0188 d = 0.0246 i = 4.39 w = 8.832	(conc. of monoamide) (conc. of diamide) (conc. of imide) (conc. of water)	monoamide diamide imide	0.42 % 0.53 % 97.96 %

It is seen that imide is by far the principal product and favoured by a factor of roughly 200 as compared to mono- and diamide. P_n according to Eq. (8) is 2.8, in line with hexamethylene diphthaloylimide being the principal component of the equilibrium mixture.

Application of Eq. (1), (2a), (3), and (4a) gives:

$$K_m = 1360,$$
 $K_d = 1830,$ $K_i = 4600,$ $K_{di} = 0.40.$

In another approach we have studied the equilibrium reaction (d) in a water-free system, using the mono functional *n*-octylamine as the basic component. Either a mixture of monoamide and amine, or a quantity of pure diamide were weighed out in a glass tube, which was then cooled in ether/dry ice, evacuated, and sealed. The tube was provided with a thin bottom allowing to break it when immersed in methanol after having been equilibrated through heating for 4 hrs. at the temperatures given below.

The amount of free amine was titrated and from it the equilibrium constant (4a) could be calculated.

In earlier experiments, when the reaction tube was quenched in silicon oil at room temp. and kept for some time before it was analyzed, it was found that a considerable shift of the equilibrium composition occurred. Diamide crystallized out and the composition of the mixture changed profoundly before analysis began. It could be confirmed that the reaction between monoamide and amine proceeds with measurable velocity at room temp. This is not the case in dilute methanol solution.

Initial composition	temp. (°C.)	$K_{di} = \frac{g}{ai}$
monoamide — amine 1:1	222	0.10
monoamide — amine 1:1	180	0.14
diamide	223	0.13

The outcome of these experiments is listed below:

The equilibrium constant in the water free system is, of course, not necessarily equal to that in the system containing water, but it is of the same order of magnitude.

5. Copolymerization with aminocaproic acid

Of numerous experiments on the copolymerization of the nylon-salt of PMA and HMD with caprolactam, only the essence will be briefly mentioned. Caprolactam to which various quantities of the PMA-HMD salt (1:1) and sometimes small quantities of other substances were added, was polymerized at 254 °C.

In the presence of 5 mole-% ordinary nylon-salt 6.6 as initiator, products completely soluble in *m*-cresol were only obtained if the addition of PMA-HMD did not exceed 5 mole-%. From 10 mole-% onwards gelled products ensued and on further addition beyond 20 mole-% even no homogeneous melts could be prepared.

If, moreover, 2 mole-% of free HMD was added at the start, gelled and insoluble products were already obtained at much lower additions of PMA-HMD, whereas in the presence of only 0.4 mole-% benzoic acid, no gelation and complete solubility were still obtained at additions as large as 38 mole-% PMA-HMD.

These results are in line with the prediction from theory (see above) that a slight excess of acid will materially counteract branching and crosslinking in polyimides.

The copolymers in question were characterized by much slower crystallization than the pure nylon 6 polymer and showed melting points rather lower than that of the latter.

Experimental part

Nylon-salts of PMA and HMD

The salt of PMA and HMD in the molecular proportion 1:1 could be prepared without difficulty in the conventional way (yield 91%). In 1% aqueous solution the pH was 3.9. Equiv. wt. by titration with alkali in water (indicator phenol red) 184.2 (theory 185). Another PMA-HMD salt in the proportion 1:2 can also be made. It tends to be contaminated by the 1:1 salt and requires recrystallization from water.

Both nylon-salts are infusible. Remarkably, the 1:2 salt is insoluble in m-cresol.

N-(n-octyl)-phthaloylimide

It is prepared by heating a mixture of equimolecular quantities of phthalic acid and *n*-octylamine in a sealed, evacuated tube for 2 hrs. at 210 °C. The two phase reaction product (imide and water) is repeatedly recrystallized from methanol. M.p. 52-54 °C.; readily soluble in many organic solvents.

N-mono(n-octyl) phthaloylmonoamide

5 mmole of the previous imide is dissolved in 25 ml. methanol and 7.5 ml. 1 N sodium hydroxide is added. After 2 hrs. at room temp., the product is acidified with 25% hydro-chloric acid. Then the monoamide crystallizes in 90% yield and is recrystallized from ligroin; m.p. 86 °C.

N, N'-di(n-octyl) phthaloyldiamide

n-octylphthaloylimide is heated with n-octylamine in the molecular proportion 1:2.2 in a sealed vessel for 4 hrs. at 210 °C. The product is dissolved in hot ethanol and diluted with a threefold volume of water. Diamide contaminated with imide crystallizes out. The imide is removed by washing with ligroin and the solid is recrystallized from ethanol under addition of water. Yield 90%; m.p. 128-129 °C.

Nylon-salt of phthalic acid and HMD

Conventional procedure; yield 90%; m.p. 193°C.

Potentiometric titrations

The only solvent permitting to titrate both dissociation steps of phthalic acid with satisfactory accuracy (from two points in the titration curve with sharp maxima in the first derivative) was a mixture of benzylalcohol and methanol in the vol. proportion 1:3. The maxima occur at pH 6.5 and 10 and corrrespond to 99% and 102% of the calc. equivalents respectively.

This solvent was then used to study the titration curves of the pure nylon-salts, monoamide and amine as well as mixtures of these of known composition with and without added phthalic acid. The results permitted to work out a procedure for the determination of the content of free amine, free phthalic acid ("first COOH") and total "second COOH" from phthalic acid and mono-amide in unknown mixtures.

Refraining from giving all details, we confine ourselves to reproduce in Fig. 1. the type of titration curve obtained with the equilibrium product referred to in section 4.



Fig. 1. Titration curve of equilibrium product obtained from a mixture of phthalic acid and its nylon-salt with HMD

After dissolution of the product, the pH of the solution was 4 (see upper curve at 0). Then the solution was titrated with 0.1064 N hydrochloric acid (upper curve from right to left) S corresponds to the end point of the reaction

$$-\mathrm{NH}_{2} + \mathrm{H}^{+} \rightarrow -\mathrm{NH}_{3}^{+} \qquad (\mathrm{I})$$

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and thus SO to the equivalency of the free amino groups in the mixture (a after the terminology of section 4).

After arrival in A at $p_{\rm H} = 1.5$, back titration with 0.0958 N potassium hydroxide was begun (see B in lower curve). BR corresponds to the neutralisation of the excess hydrochloric acid and R corresponds to S in the upper curve. Continuing the addition of alkali, the reaction

$$-COOH + OH^{-} \rightarrow -COO^{-} + H_2O \qquad (II)$$

as pertaining to the first dissociation step ("first carboxyls") of phthalic acids commences and is finished in Q at pH = 6.5. Consequently, RQ represents the equivalency of one carboxyl (the "first" one) of the free phthalic acid.

Further, QT corresponds to the equivalency of two reactions in addition (between which no transition point is observable on the curve), namely the reversal of Eq.(I) and the reaction (II) for the "second" carboxyl in phthalic acid and monoamide. Expressing the titration equivalents in the concentrations in mole/kg. as they occur in the reaction product, we have: QT = SO + RQ + monoamide-carboxyl = (a + f + m). Consequently, PT represents c (total carboxyl). Condensed:

$$SO = a; RQ = f; QT = a + f + m; PT = c = 2f + m$$

¹⁾ Brit. P. 570.858 (1942), DuPont de Nemours.

²⁾ U.S.P. 2.710.853 (1953), DuPont de Nemours.

³⁾ U.S.P. 2.867.609 and 2.880.230 (1955), DuPont de Nemours.